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Application of Air Cathode Microbial Fuel Cells for Energy Efficient Treatment of Dairy Wastewater

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Abstract

Microbial Fuel Cells (MFCs) offer a promising new solution for wastewater treatment due to their advantageous characteristics: lower energy demand and less excess sludge compared to the conventional activated sludge wastewater treatment technology. In this study, two systems of single chamber air cathode MFCs with a working volume of 14 L were investigated for the energy efficient treatment of dairy wastewater. Biomass-originated carbon cathode and noble-metal free cathode catalyst were applied to meet the demand for a lower investment cost. Influent chemical oxygen demand (COD) was in the range of 900 to 3830 mg L^{-1}, while hydraulic retention time was ~ 2.4 days. Systems provided 156 mW m^{-3} and 170 mW m^{-3} maximum power densities and coulombic efficiencies of 11.5 % and 12.8 % in average. Organic removal efficiency of 71.1 ± 8.0 % was observed when influent COD was between 900 and 1500 mg L^{-1}, however effluent quality and removal efficiency (67.9 ± 12.6 %) deteriorated as influent COD was increased (1500 – 3830 mg L^{-1}). At high influent CODs (over 3000 mg L^{-1}), an organic elimination rate of 0.82 ± 0.11 kg COD m^{-3} d^{-1} was calculated, that can be considered as the upper limit of organic removal in the systems. Based on the results, MFCs may offer a potential solution for small-scale dairy factories for the pretreatment of their effluent to meet the criteria for wastewater discharge to sewer systems. The modular MFC design also facilitates to tailor the system to actual capacity requirements.

Keywords

microbial fuel cell, air cathode, dairy industry wastewater, wastewater treatment

1 Introduction

Specific type of bioreactors, the microbial fuel cells (MFCs), are able to convert the chemical energy of biodegradable organic compounds into bioelectricity by the metabolism of the so called exoelectrogenic bacteria. Although the first observation of current generating microbes is dated back to the beginning of the 20th century [1], the progress in materials and biotechnology promoted the potential applications of MFCs from the late 1990s, when conventional fuel cells became of more interest.

MFCs can be applied as green power source and used as biosensors to measure the biodegradable organics content of a sample or to reveal the presence of toxic compounds [2–4]. Specific features facilitate the application of MFCs as promising new wastewater treatment technology: compared to the conventional aerobic activated sludge treatment, MFCs have considerably lower energy demand, they produce less excess sludge while the organics removal efficiency is comparable [5, 6].

In an MFC, the biodegradation of organic matter carried out by the exoelectrogenic bacteria (e.g. members of genera *Shewanella* and *Geobacter*) takes place in the anode compartment, where strictly anaerobic conditions have to be maintained. In the absence of dissolved terminal electron acceptors (e.g. oxygen, nitrate, nitrite, sulfate), electrons obtained by the oxidation of organics are transferred to the solid conductive surface of the anode.

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This transport is established either indirectly by electron shuttle molecules (e.g. flavins, pyocyanin), or directly by specialized conductive nanopili [7].

Utilizable power can be harvested when electrons migrate from the anode surface through a circuit to the cathode, where the oxygen reduction reaction (ORR) takes place. The required protons are transported to the cathode surface generally via a selective ion-exchange membrane, that also prevents oxygen diffusion into the anolyte.

By applying a so-called air cathode (generally a porous carbon material layered on the membrane), neither energy intensive aeration nor cathode chamber with catholyte is needed, oxygen for ORR is supplied by diffusion directly from air. Thus, air cathode MFCs are compact, easy to handle systems with the most energy efficient operation [8].

Since the millennium, a paradigm-shift took place in the field of wastewater treatment. As a result, wastewater is now considered as a source of reusable water, energy and other valuable nutrients (e.g. nitrogen, phosphorous) [9, 10]. Conventional treatment technologies have energy- and cost-related limitations, so innovative new solutions are required that can exploit effectively the available resources in wastewaters. Due to their advantageous characteristics, MFCs are promising candidates as standalone units or integrated with other treatment processes [11].

Several types of industrial wastewaters (e.g. from agro-food field) are rich in biodegradable organics, therefore they are appropriate media for exoelectrogens as it has been reported in several studies recently [6, 12, 13]. Dairy industry produces effluents in large volume, containing carbohydrates, lipids, proteins and inorganic components as well, with raw COD (chemical oxygen demand) values from 0.5 g L^{-1} to as high as 140 g L^{-1} [14, 15]. There are numerous ways by which valorization of this special waste is possible: whey protein production, SCP fermentation, organic acid fermentation (e.g. lactic acid, propionic acid), utilization in anaerobic digesters [16], or using it for the co-treatment of carbon deficient domestic wastewaters [17]. Yet, for most diary industry companies, it is essential to integrate a capable on-site treatment technology. Since this complex media is suitable for MFCs, multiple studies focused on the applicability of MFCs in the sustainable management of dairy wastewater.

Using a dual-chamber MFC with net anodic compartment volume of 435 cm^3 and 10.5 h hydraulic retention time (HRT), 82 % average organic removal rate and a power density of 26.5 W m^{-3} were achieved while treating cheese factory wastewater with an organic loading rate (OLR) of 0.6-7.9 kg COD m^{-3} d^{-1} into the cell [18]. Another study found 1.9 W m^{-3} power density and 63 ± 5 % maximum COD removal efficiency in a dual-chamber MFC with a working volume of 350 mL. In this experiment, a synthetic waste was used that simulated average dairy wastewater with COD values from 1500 to 5000 mg COD L^{-1}, and it was fed continuously into the anode chamber with a HRT of 8.4 h [19]. A 200 mL single chamber MFC inoculated with *Escherichia coli* K12 operated in fed batch mode showed a COD removal efficiency as high as 95.45 % while using diluted real dairy wastewater with 500–2000 mg COD L^{-1}. Maximum power density of the cell achieved by a platinum catalyzed air cathode (0.5 mg cm^{-2} Pt/C on carbon cloth) was 1.05 W m^{-2} that equals to 26.25 W m^{-3} [20] comparable with previous results, though the studies presented earlier did not use catalyzed cathodes. By utilizing real high-strength dairy wastewater (5209 ± 113 mg L^{-1} of total COD), a COD removal efficiency of 62 % and 90 % reduction of biochemical oxygen demand were attained along with 1.45 W m^{-3} power density in a 500 mL tubular air cathode MFC inoculated with *Shewanella oneidensis* MR-1 and *Clostridium butyricum* [21].

Investigations focusing on larger scale MFC systems are rather rare, but there are some encouraging examples. A modularized MFC system with 300 L anodic working volume was tested for municipal wastewater treatment (80 – 400 mg COD L^{-1}). During the one-year long operation, effluent concentrations remained under 50 mg COD L^{-1} resulting in a COD removal efficiency of 70–90 % while generating 7–60 W m^{-3} [22]. A submergible 255 L MFC module was fed with municipal wastewater containing industrial discharges as well for 98 days. A power density of 317 mW m^{-3} and COD removal of 41 ± 16 % were reached when the HRT was set to 1.8 days. However, high salt content caused inorganic fouling and severe decline in power output over time [23]. A stacked MFC system consisting of six air cathode MFCs each with a volume of 120 L was fed with high-strength wastewater. When the HRT was set to 36 h a COD removal efficiency of 87.29 % ± 7.28 % was achieved while the system produced a maximum power of 61 mW [24]. Using swine wastewater as influent, a system composed of 12 single chamber MFCs with a total volume of 110 L reached a COD removal efficiency of 65 % and a power density of 800–933 mW m^{-3} with a HRT of 4 h [25]. Results are summarized in Table 1.

Despite the promising results, large scale MFC applications are still facing several obstacles: general experience is that with the scale-up, the specific parameters referring to the performance (power density, specific organic elimination rate) are deteriorating. Also, long-term stability problems may occur (e.g. membrane fouling). High capital investment costs due to expensive structural materials such as precious-metal based cathode catalysts [6, 22] are also hindering the full-scale application of MFCs.

Thus, further efforts should be made for the development of alternative materials like carbon aerogels [26] and innovative membrane solutions [27].

In this study, two single chamber air cathode MFC systems with a working volume of 14 L were assembled to investigate their organic removal capability with artificial dairy wastewater. Less expensive materials (e.g. carbonized coconut shell originated cathode with noble metal free catalyst) were selected and applied to meet the demand for a lower investment cost.

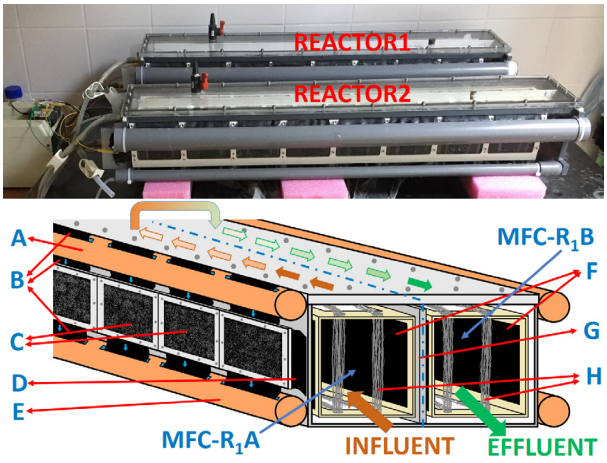

Fig. 1 Top: the two 14 L air cathode MFC systems (Reactor1 and 2), Bottom: scheme of Reactor1, A: water container, B: wetting carbon cloth, C: air cathodes, D: current collecting carbon cloth, E: spent water collector, F: carbon anodes, G: PVC separator, H: carbon fiber bundles

2 Materials and methods

2.1 MFC architecture, data collection

The structure of the two 14 L air cathode systems (Reactor1 and Reactor2) is based on the works of Fedorovich et al. [28] and Dimou [29]. Assembly of the reactors with dimensions of 100 cm × 30 cm × 22 cm was carried out using PVC parts and a transparent lid made of acrylic material.

A 14 L reactor (Fig. 1) consists of two 7 L sub-reactors connected hydraulically in series. In each sub-reactor, an MFC was formed by placing a prefabricated anode structure in it and by creating air cathodes on the outer side of the anodic compartment. As a result, Reactor1 consisted of sub-reactors MFC-R_1A and R_1B, while Reactor2 consisted of MFC-R_2C and R_2D. A sealable hole for reference electrode and a valve for excess gas removal were placed on the acrylic top. Two PVC tubes containing water for the adequate wetting of air cathodes and two tubes for collecting spent water were secured on the sides. Without the extra wetting, electrical parameters (e.g. current, power output) provided by the systems deteriorated within a day. For influent and effluent, two tube connection points were formed on the same side.

Reactor1 and Reactor2 were operated in parallel, but sub-reactors were connected hydraulically in series. The waste stream was fed into the first sub-reactors (MFC R_1A and R_2C) via silicone tubing by a peristaltic pump (Masterflex®, L/S Model 7523-37). Flowing through the first sub-reactors, the wastewater entered MFC R_1B and R_2D across a small opening on the PVC separator at the end of the reactor opposite to the feeding point. Flowing through the second sub-reactors, effluent left the systems on the entry side.

Table 1 Summary of MFC design, net anodic volume (Vnet), hydraulic retention time (HRT), wastewater strength, chemical oxygen demand (COD) removal efficiency and power density values of previous studies with dairy and municipal wastewater

MFC design	V_{net} (L)	HRT (h)	WW strength (mg COD L^{-1})	COD removal efficiency (%)	Power density (W m^{-3})	Reference
Dual-chamber	0.435	10.5	~ 700–3400	82	26.5	[18]
Dual chamber	0.35	8.4	1500–5000	63 ± 5	1.9	[19]
Single chamber air cathode	0.2	fed batch	500–2000	95.45	26.25	[20]
Tubular air cathode	0.5	semi-continuous feed	5209 ± 113	62	1.45	[21]
Dual chamber, modularized	300	2	80–400	70–90	7 - 60	[22]
Multi-panel air cathode	255	11.5–42.6	~ 100–260	41 ± 16	0.317	[23]
Stacked air cathode	720	18 / 36	976–8220	78 ± 19 / 87 ± 7	7.29–3.79*	[24]
Single chamber air cathode	110	4	~ 500–600	65	0.8 ± 0.93	[25]

*mW m^{-2} cathode surface

The complex three-dimensional structure of the anodes consisted of a PVC frame with dimensions of 96 × 10 × 8 cm, carbon cloth (Plain Carbon Cloth untreated, Fuel Cell Store, USA) that covered the two sides of the frame, activated carbon granules (AquaSorb HS, Jacobi, UK) glued to the carbon cloth with conductive glue (graphite powder and polystyrene binder) and two carbon fiber bundles (Zoltek PX35, Toray Group, USA) that were fixed on the frame [29]. Conductive anode materials were connected with titanium wire to a stainless steel screw passing through reactor frame.

Porous ceramic plates (6 cm × 8 cm) with ion exchange polymer (Fumion®) in the pores were used as proton exchange membrane (PEM). Eight plates were used in an MFC sub-reactor, with a total proton transporting surface area of 384 cm^2.

For each plate of PEM, an air cathode with a structure consisting of 4 layers was applied [30]. Carbon cloth was laid lengthwise on the side of the cell in contact with the membrane surfaces, connecting the eight cathodes electrically. Current collecting wires were fixed with stainless steel screws to this layer. The second layer, extending through the frame of the air cathode upwards and downwards was made of the same carbon cloth, and was immersed in tap water, providing aqueous medium for ORR. 50 mL carbonized coconut shell granules (diameter cca. 2–4 mm) treated with 5 % solution of Fe(II)-phtalocyanin in N-methylpyrrolidone as previously described by Zhao et al. [31] was added. Finally, all the aforementioned parts were squeezed together and fixed to the side of the cell with a plastic mesh and a PVC frame.

The electric circuit of an MFC consisted of copper cables connecting the anode to the air cathodes and an adjustable external resistance (helipot, 0–10 kΩ). Voltage on the external resistance was measured and registered in every minute with data collection device (Graphtec midi logger GL840 oscilloscope). Electrode potentials were determined against Ag/AgCl reference electrode (XR300, Radiometer analytical).

2.2 MFC operation

2.2.1 Composition of the media

Artificial wastewater introduced to the systems contained salt components to increase buffer capacity and to simulate real wastewater properties: 0.31 g L^{-1} $NaHCO_3$, 0.03 g L^{-1} NH_4Cl, 0.013 g L^{-1} KCl, 0.42 g L^{-1} NaH_2PO_4, 0.69 g L^{-1} Na_2HPO_4*12 H_2O (a.r., Molar Chemicals) dissolved in tap water [32]. The carbon source was sodium acetate with a total chemical oxygen demand of ~500 mg L^{-1} during inoculation period, while commercially available milk was used during adaptation and experimental phase 1 and 2 in various quantity to reach the desired organic loading rate (OLR, kg COD m^{-3} d^{-1}). A 40 L plastic container was used to store artificial wastewater (AW) in a fridge (8°C) to minimalize microbial degradation prior to feeding.

2.2.2 Inoculation

Primary settled sludge from a domestic wastewater treatment plant (South-pest WWTP) was collected as inoculum. For the inoculation period acetate, the most widespread substrate for MFCs was used: the sludge was diluted with AW containing 4.1 g L^{-1} sodium acetate to ~1 g TSS L^{-1} (total suspended solids). Both systems were filled with the inoculating suspension and sealed. The feeding of fresh AW described in Section 2.2.1 was started after a week to wash out the remaining suspended solids and to provide acetate rich media for the systems. Within the ~4 weeks long inoculation period the voltage values increased and stabilized at 0.45–0.5 V in each MFC while external resistances were set to 1000 Ω.

2.2.3 Polarization measurements

The electric parameters of the cells were determined by polarization tests (e.g. internal resistance values were derived from the slope of current versus measured voltage plot). Two-step tests were carried out to eliminate the effect of voltage hysteresis: at first the adjustable external resistance was increased from 0 to 10 000 Ω by defined steps, after that current was cut to measure open circuit voltage (OCV) and finally R_{ext} was decreased from 10 000 to 0 Ω using the same steps. Polarization curves were obtained by calculating the average voltages for each external resistance value.

2.2.4 Analytics and coulombic efficiency

Chemical oxygen demand (COD) was measured according to international standards [33].

Coulombic efficiency (CE) of a reactor was calculated from organic elimination rate (OER, kg COD m^{-3} d^{-1}) and the total charge (C) flown through the two external circuit of the sub-reactors under a period of time, based on the work of Logan [8].

2.2.5 Operation of the experimental setup

The two 14 L air cathode systems were operated indoors at room temperature. Feeding rate provided by the peristaltic

pump was 4 mL min^{-1}, resulting in a hydraulic retention time of ~2.4 days during the whole experiment. Fresh artificial wastewater was prepared every day.

Once the voltage values of MFCs stabilized and the inoculation period was finished, the use of milk (1.5 % fat content, Alföldi Tej Ltd.) containing AW with a COD value of ~500 mg L^{-1} started. An adaptation period of 3 weeks was carried out to ensure that the change of carbon source does not affect the results of the experiment. Polarization measurements were carried out during this phase to determine basic electric parameters and to verify that the systems reached a stable operating condition. As no considerable shift was observed for 2 weeks, the adaptation period was ceased and experimental phase was started by increasing influent organic content. Simultaneously, R_{ext} was decreased to 50 Ω, as polarizations revealed that the cells reach their maximum power output close to this value. During experimental phase 1, influent COD was between 900 and 1500 mg L^{-1}, while under experimental phase 2, the influent COD was ranging from 1500 to 3830 mg L^{-1}. Characteristics of all phases are summarized in Table 2.

The COD of each influent batch coupled with effluent samples collected three days later (as HRT was 2.4 days) were used to determine organic elimination rate and organic removal efficiency (%) of a system.

3 Results and discussion

3.1 Performance characteristics of the MFCs

Voltage values measured in the four MFCs during inoculation and adaptation period is depicted on Fig. 2. Following a latency phase of ~2 days, a two-step exponential increase of voltage was observed before reaching the plateau at the end of the fourth week. The specific shape was possibly the result of early microbial community shifts in the midst of anodic biofilm formation. Having the inoculation period finished, investigation of electrical performance of the cells was carried out by polarization measurements during adaptation period, as electrochemical properties and biofilm composition of the cells can change even after the stabilization of voltage output [34].

Table 2 Summary of the applied external resistance (R_{ext}, Ω), type of substrate (S), influent chemical oxygen demand (COD, mg O_2 L^{-1}), organic loading rate (OLR, kg COD m^{-3} d^{-1}) and hydraulic retention time (HRT) of the four phases

	Inoculation phase	Stabilization phase	Experimental phase 1	Experimental phase 2
R_{ext}	1000	1000	50	50
S	Acetate	Milk	Milk	Milk
COD	500	500	900–1500	1500–3830
OLR	0.21	0.21	~0.36–0.62	0.62–1.58
HRT	2.4 days			

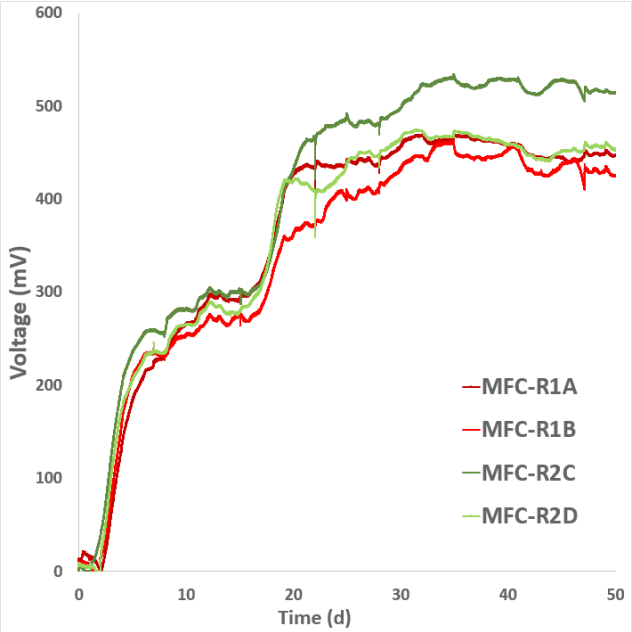

Fig. 2 Voltage of the MFCs during inoculation and adaptation period

Internal resistances (R_{int}, Ω) and maximum power densities (the maximum power output per MFC volume, Pd_{max}, mW m^{-3}) were determined regularly with polarization measurements. Results are summarized in Table 3. Relative standard deviations of both parameters were rather low (less than 12 % in every case) and no trend in data was observable in the adaptation phase, thus the systems were considered stable and the stepwise increase of biodegradable organic content of dairy AW started with experimental phase 1. As a result, no significant change ($\alpha = 0.05$) in electrical characteristics was observed for MFC-R_1A and R_2C (first sub-reactor chambers), while average R_{int} decreased (by 20 % and 36 %) and average P_{dmax} values increased (by 51 % and 40 %) significantly in MFC-R_1B and R_2D (second sub-reactor chambers). Also, the shift in electrode and cell potentials of second sub-reactors suggests that both systems were underloaded before, and their operational capabilities were exploited only when OLR was increased. This is demonstrated by Fig. 3, where typical polarization curves of cell R_1A and R_1B from adaptation and experimental phase 1 are depicted. During experimental phase 2, no significant change ($\alpha = 0.05$) occurred in the discussed parameters despite further increasing OLR, thus electric parameters became practically independent from the OLR and MFCs reached their power producing maximum.

Table 3 Average internal resistance (R_{int}) and maximum power density (Pd_{max}) values along with standard deviation (SD) and relative standard deviation (RSD) of the four MFCs during adaptation (adap.) and experimental (exp.) phase 1. Average electrode potentials (E_{anode} and $E_{cathode}$) against Ag/AgCl ref. electrode and cell (E_{cell}) potentials are listed (R_{ext} = 50 Ω)

MFC-		R_1A	R_1B	R_2C	R_2D
		R_{int} (Ω)			
Average (n = 5)	adap.	71.8	97.3	57.8	92.0
	exp.	72.7	77.3	59.7	58.7
SD	adap.	3.0	11.5	5.7	5.8
	exp.	3.2	7.0	3.1	3.5
RSD (%)	adap.	4.2	11.8	9.9	6.2
	exp.	4.4	9.1	5.1	6.0
		Pd_{max} (mW m^{-3})			
Average (n = 5)	adap.	169.3	96.0	169.8	122.3
	exp.	167.6	144.7	166.3	171.8
SD	adap.	13.9	8.0	19.5	5.6
	exp.	10.8	5.5	8.1	20.2
RSD (%)	adap.	8.2	8.4	11.5	4.5
	exp.	6.4	3.8	4.9	11.8
		E_{anode} (mV)			
Average (n = 7)	adap.	-392.6	-350.4	-378	-359.6
	exp.	-394.6	-388.9	-383.2	-386.5
		$E_{cathode}$ (mV)			
Average (n = 7)	adap.	-172.9	-162.4	-161.7	-167.5
	exp.	-172.1	-149.3	-152	-150.2
		E_{cell} (mV)			
Average	adap.	219.7	188	216.3	192.1
	exp.	222.5	239.6	231.2	236.3

Average Pd_{max} values of Reactors 1 and 2 (calculated from the average power output of the two MFCs of the sub-reactors) are 156 and 170 mW m^{-3}, respectively. These results fit with previous studies in this area (0.02–27 W m^{-3} [12, 18]). The high variability of Pd_{max} values in literature may be due to different MFC structures, effective volumes and electrode surface areas. Also, scale-up of MFCs often results in the decrease of power density [35].

3.2 Organics removal in the systems

Influent and effluent COD concentrations are presented on Fig. 4. With influent of the adaptation period (500 mg COD L^{-1} or OLR of 0.21 kg COD m^{-3} d^{-1}), an organic removal efficiency of 87.9 ± 3.5 % in Reactor 1 and 88.6 ± 1.5 % in Reactor 2 was achieved (see on Fig. 5). This means an average organic elimination rate of 0.18 kg COD m^{-3} d^{-1}, and effluent COD values were under the

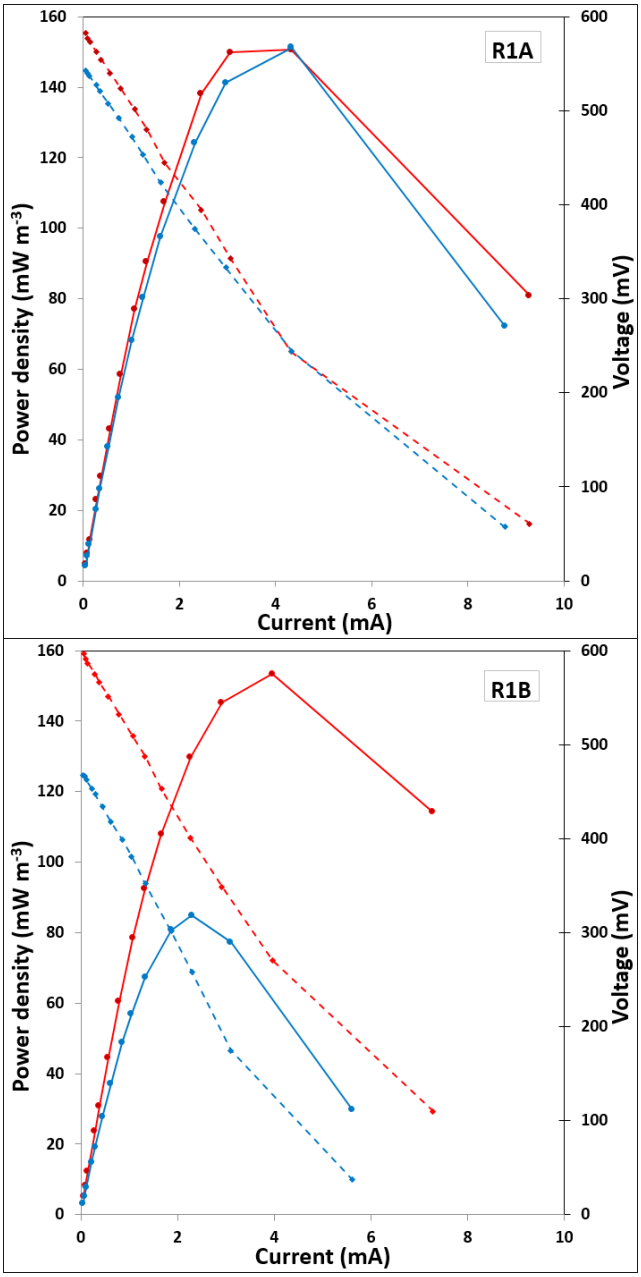

Fig. 3 Typical polarization curves of MFC-R_1A and R_1B from adaptation (blue) and experimental phase (red) (Dashed line–voltage)

Hungarian discharge limit of 110 mg L^{-1} applicable for dairy wastewaters [36]. Average coulombic efficiencies during adaptation phase were found to be 29.8 % (RSD 4.8 %) and 30.7 % (RSD 2.4 %) for the two Reactors.

Effluent quality along with organic removal efficiency deteriorated as the influent COD was increased during experimental phase 1. Removal efficiency in Reactor1 decreased to 74.6 ± 7.3 % and to 67.6 ± 8.9 % in Reactor2. These values are significantly ($\alpha = 0.05$) lower than in adaptation period, however, OER nearly doubled (increased by 87 %) and reached 0.34 kg COD m^{-3} d^{-1} in average.

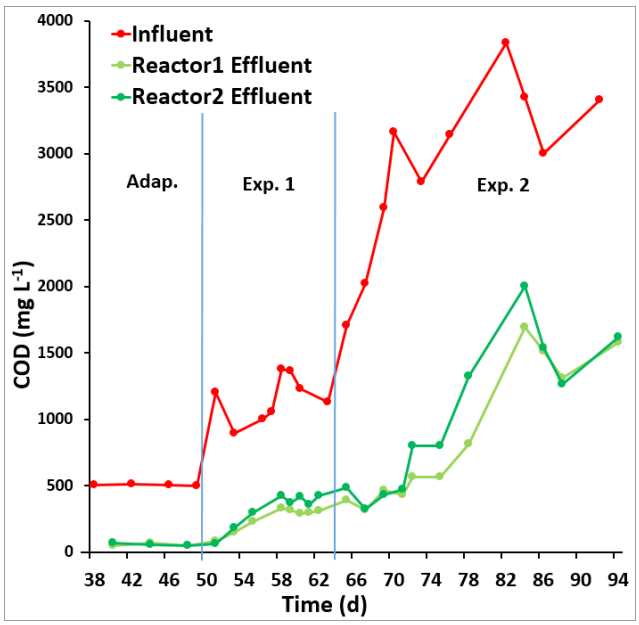

Fig. 4 Average COD of influent along with effluent values. Blue lines represent the beginning of a new phase. Adap. stands for adaptation phase, Exp. 1 and Exp. 2 for experimental phase 1 and 2

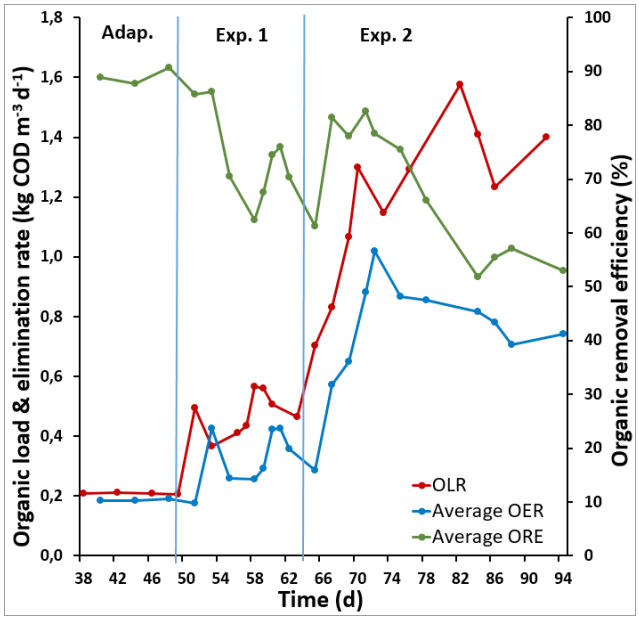

Fig. 5 Organic loading rate (OLR, kg COD m^{-3} d^{-1}), average organic elimination rate (OER, kg COD m^{-3} d^{-1}) and average organic removal efficiency (ORE, %). Adap. stands for adaptation phase, Exp. 1 and Exp. 2 for experimental phase 1 and 2

Coulombic efficiencies of 18.5 ± 3.1 % and 20.4 ± 4.1 % were calculated, that means an average decline of 35.7 % in this parameter, indicating that the role of non-exoelectrogenic anaerobic processes in organics removal escalated. Yet, the greater increment in OER and the observed escalation of electric parameters in the second sub-reactors of the systems indicate that the increased OLR leads to enhanced substrate removal as well as power production.

During experimental phase 2, influent's organic content was increased to as high as 3830 mg COD L^{-1} (OLR of 1.58 kg COD m^{-3} d^{-1}). As a result, average removal efficiency fell to the range of 67.9 ± 12.6 %, with a minimum value of 51.8 %. Observed removal efficiencies are in accordance with those (58–95.5 % COD removal in various MFCs using dairy wastewater with COD values from 650 to 4440 mg L^{-1}) summarized by Marassi et al. [21]. Although average OER further increased and peaked at 1.02 kg COD m^{-3} d^{-1}, it has reached its plateau during phase 2 as it can be observed on Fig. 5. If only the results of influents with a COD higher than 3000 mg L^{-1} are taken into account, the average OER is 0.82 ± 0.11 kg COD m^{-3} d^{-1} (140 % increase compared to experimental phase 1). This can be considered as the upper limit of organic removal in the systems presented in this study.

Average coulombic efficiencies of experimental phase 2 were 7.5 % and 8.0 % for the two reactors. These results show a 60.1 % reduction of CE in average, what roughly compensates the 140 % increment of OER, suggesting that exoelectrogenic activity has not accelerated despite the surplus of biodegradable organics and that increased OER is solely the result of accelerated non-exoelectrogenic anaerobic activity. This hypothesis is supported by cell voltages, P_{dmax} and R_{int} values that have not changed significantly ($\alpha = 0.05$) compared to phase 1.

Lowest CEs (6.1–7.4 %) were observed at the highest OLRs. This phenomenon with similar results was described by Callegari et al. [18]. For the whole experimental phase, average CEs were found to be 11.5 % and 12.8 %. CEs presented in this study are in accordance with previous experiments that were using dairy wastewater as influent, but MFCs with significantly smaller effective volume (< 0.5 L) [18, 19, 21]. At the same time, the average of the produced energy related to the removed substrate in COD (CODR) was 38.5 J kg $CODR^{-1}$ in experimental phase 1 and 17.4 J kg $CODR^{-1}$ in experimental phase 2. These values are comparable to the results of a previous study (40.4–144.8 J kg $CODR^{-1}$) treating vegetable waste in a considerably smaller (0.5 L) MFC [37].

As it can be observed on Fig. 4, effluent values exceeded discharge limit during the whole experimental phase, however, the COD requirement for discharge into the public sewers (1000 mg L^{-1} [36]) was not exceeded when

influent was below 3000 mg COD L^{-1}. Generally, larger factories handle their wastewater on site before releasing it into natural water bodies, but numerous small-scale producers are using public sewers, thus this technology may offer an easy to handle solution for pretreatment to meet governmental regulations.

The design of the applied reactors enables the modular application, so a complex system using multiple units can be tailored to a given dairy wastewater quality and quantity. In this case, effluent COD values and removal efficiencies could have been improved by connecting the two reactors hydraulically in series, thus increasing the total hydraulic retention time. Likewise, electrical parameters as well as power output could have been increased by connecting MFCs electrically in series.

4 Conclusions

Two 14 L reactors each containing two scaled-up single chamber air cathode MFCs were investigated for the treatment of dairy wastewater with influent COD concentration from 900 to 3830 mg L^{-1}.

The systems provided 156 mW m^{-3} and 170 mW m^{-3} maximum power densities. At high influent concentrations (>3000 mg COD L^{-1}, 1.34 kg COD m^{-3} d^{-1} OLR in average), an organic elimination rate of 0.82 ± 0.11 kg COD m^{-3} d^{-1} was obtained, that can be considered as the upper limit of organic removal in one reactor. At the same time, average organic removal efficiency was 67.9 %, and 17.4 J kg $CODR^{-1}$ energy conversion efficiency was observed.

Results suggest that the investigated MFCs may offer an easy to handle solution for small-scale dairy factories to pretreat their waste streams prior to discharge into public sewers to meet governmental regulations, and based on the observed efficiency parameters, an on-site modifiable system tailored to local needs can be assembled by using several reactors presented in this paper.

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